



# Experimental evidence for water formation on interstellar dust grains by hydrogen and oxygen atoms

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## Abstract

**Context.** The synthesis of water is one necessary step in the origin and development of life. It is believed that pristine water is formed and grows on the surface of icy dust grains in dark interstellar clouds. Until now, there has been no experimental evidence whether this scenario is feasible or not on an astrophysically relevant template and by hydrogen and oxygen atom reactions.

**Aims.** We present here the first experimental evidence of water synthesis by such a process on a realistic grain surface analogue in dense clouds, i.e., amorphous water ice.

**Methods.** Atomic beams of oxygen and deuterium are aimed at a porous water ice substrate ( $\text{H}_2\text{O}$ ) held at 10 K. Products are analyzed by the temperature-programmed desorption technique

**Results.** We observe production of HDO and  $\text{D}_2\text{O}$ , indicating that water is formed under conditions of the dense interstellar medium from hydrogen and oxygen atoms. This experiment opens up the field of a little explored complex chemistry that could occur on dust grains, believed to be the site where key processes lead to the molecular diversity and complexity observed in the Universe.

**Key words.** astrochemistry – ISM: molecules – ISM: dust, extinction – methods: laboratory

## 1. Introduction

Water, the spring of life (Brack 2002), is the most abundant molecule in biological systems, and it is almost certainly of extraterrestrial origin. Water has been detected, in gaseous or solid form, in numerous astrophysical environments such as planets, comets, interstellar clouds and star forming regions where strong maser emission can be also observed (Ehrenfreund et al. 2003; Dartois 2005). Amorphous water ice was directly detected in dark interstellar clouds through infra-red absorption

(Leger et al. 1979). During the formation of stars deep inside molecular clouds, gas and dust become part of the infalling material feeding the central object. Part of this gas and dust grains, covered with icy mantles (mainly composed of water), ends up in the rotating disks surrounding young stars and forms the basic material from which icy planetesimals and later planets, together with comets in the external regions, are formed (van Dishoeck 2004). While the means of delivery of water to Earth remain a subject of debate (Morbidelli et al. 2000), the synthesis of water in the Universe is a fundamental link in establishing our origins. Water molecule formation in the gas phase is not efficient enough to reproduce the observed abundances in dark clouds, especially in its solid form (Parise et al. 2005; Ceccarelli et al. 2007). Therefore water ice must form directly on the cold interstellar grains and not as a condensate after being formed in the gas phase. A complete review of the processes involved both in the gas and solid phase has been recently published (Tielens 2005). It was suggested many years ago that interstellar dust grains act as catalysts (Oort & van de Hulst 1946; van de Hulst 1946). Starting from simple atoms or molecules such as H, O, C, N, CO, grains are believed to be chemical nanofactories on which more complex molecules are synthesized leading eventually to prebiotic species produced concurrently by surface reactions and by UV photons and cosmic rays irradiation, as already shown long ago (Hagen et al. 1979; Pirronello et al. 1982). The most volatile species may be released in the gas phase upon formation (Garrod et al. 2007), while the refractory ones remain on the grain surface, building up a so called “dirty icy mantle”, and at least partially may be sputtered by the heavy component of cosmic rays (Johnson et al. 1991). Such mantles, having a typical thickness of a hundred monolayers, are mainly composed of water, the most abundant solid phase species in the Universe. Under dark cloud conditions, except for the very first monolayer that has to grow on bare silicate or carbonaceous grains (Papoula 2005), most water molecules should be subsequently synthesized on a surface mainly composed of water.

Chemical models including water formation on grain surfaces were proposed years ago by (Tielens & Hagen 1982). They suggested that H<sub>2</sub>O formation would be initiated by H-atoms reacting with O, O<sub>2</sub> and O<sub>3</sub>, although the O<sub>3</sub>+H pathway was considered the most effective and O<sub>2</sub> would play more a catalytic role. Recent Monte Carlo simulations (Cuppen and Herbst 2007) show that while the main route to water formation on cosmic dust grains in diffuse and translucent clouds is the reaction H + OH, in dense clouds the principal source of H<sub>2</sub>O is the reaction between H<sub>2</sub> and OH. This study also emphasizes the non-negligible contribution from the H + H<sub>2</sub>O<sub>2</sub> reaction (H<sub>2</sub>O<sub>2</sub> being a product of the H + O<sub>2</sub> pathway) and the unusual high abundance of reactants such as OH and O<sub>3</sub>. Interestingly, another code by (**author?**) (Parise 2004) proposed a water formation scheme where O<sub>3</sub> molecules react with H- or D-atoms to form OH or OD, and subsequently the reaction H<sub>2</sub> + OH/OD leads to H<sub>2</sub>O/HDO. It should be noted that this scheme was in part also constrained by the observed abundances of deuterated species.

In previous laboratory works, (Hiraoka et al. 1998) succeeded in producing water molecules from the reaction of H- and O-atoms initially trapped in a N<sub>2</sub>O matrix. Very recently (Miyauchi et al. 2008) investigated the reaction between cold H-atoms and an O<sub>2</sub> ice at 10 K and demonstrated the production of H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O molecules and estimated the efficiency of the reactions. (Ioppolo et al. 2008) did a similar experiment but with varying O<sub>2</sub> substrate temperatures. They confirmed the production of H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O, made an estimate of the reactions efficiency and also drew conclusions upon the temperature dependence of the amount of

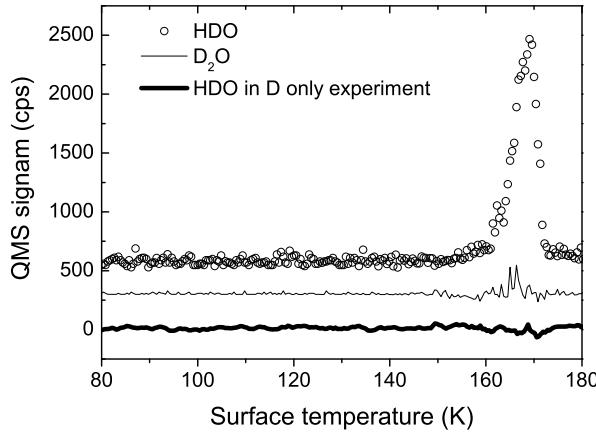
species produced. These two experiments dealt with the H<sub>2</sub>O production pathway in which O<sub>2</sub> is the species consumed to produce water as shown in preliminary experiments by our group (Momeni et al. 2007; Matar et al. 2008)

In the present study, the formation of water is studied for the first time using hydrogen and oxygen atoms interacting on the surface of an amorphous solid water (ASW) ice film, hence under conditions that are much more relevant to the interstellar medium. The aim of this first attempt to synthesize water under conditions close to those encountered in dense clouds was to investigate how water formation continues on the icy surfaces of cosmic grains and to give an estimate of the efficiency of the chemical path(s) actually active.

## 2. Experimental procedures

Experiments were performed with the FORMOLISM set-up (Amiaud et al. 2006). In brief, a copper sample surface whose temperature can be controlled by computer in the 8-800 K range is maintained under UHV conditions; on it an amorphous solid water ice substrate, on which water formation is studied, is prepared in two steps. First, a 100-layer film of non-porous ASW ice is first deposited at 120 K (Kimmel et al. 2001), then an overlayer of 10 layers of porous ASW ice is grown at 10 K. The underlying non-porous water film isolates the ice layer from the copper substrate (Engquist et al. 1995). This double ASW ice film is annealed to 90 K prior to each experimental run in order to avoid any further collapse of the pores between 10 and 80 K in the subsequent temperature-programmed desorption (TPD) experiments (see below). In fact, the species D<sub>2</sub>, O, O<sub>2</sub> used in this experiment will be thoroughly evaporated by 90 K and thus before any rearrangement in the porous structure of the ice template.

The annealed water ice substrate is still porous (Kimmel et al. 2001) and mimics an amorphous ice processed by UV and cosmic rays (Palumbo 2006) that is thought to constitute the icy mantle of interstellar grains. By using an architecture with two separate channels (Pirronello et al. 1997), each consisting of a triply differentially pumped beam line, two atomic beams of O and D are aimed at the ASW ice substrate held at 10 K. Atoms are produced by dissociation of O<sub>2</sub> and D<sub>2</sub> in microwave discharges. The dissociation efficiency of the oxygen beam is typically 40%, meaning that for 100 O<sub>2</sub> molecules that initially feed the discharge, 60 O<sub>2</sub> molecules and 80 O atoms will finally reach the cold target. Trace quantities of residual gases (i.e., CO, N<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>O) are present in the beam, although neither O<sub>3</sub> nor deuterated compounds were detected. The D beam has a 60% dissociation efficiency, and no UV photons from the D<sub>2</sub>-discharge plasma can reach the water ice sample. The purity of the beams was checked with a rotatable quadrupole mass spectrometer (QMS) that intercepted the incoming beam. The O- and D-beams have a flux of 10<sup>12</sup> atoms/cm<sup>2</sup>/s and 5 × 10<sup>12</sup> atoms/cm<sup>2</sup>/s, respectively. After concurrent or sequential injection of the beams, a TPD is performed at a heating rate of 20 K/minute from 10 K to 200 K and simultaneously the desorbing species are monitored with the QMS. The signals of mass 19 (HDO) and mass 20 (D<sub>2</sub>O) presented here are corrected by subtracting the contribution of the H<sub>2</sub>O water substrate, which naturally includes some isotopes.



**Figure 1.** TPD profiles of  $D_2^{16}O$  (thin line) and  $HD^{16}O$  (circles) after irradiation of the water substrate ( $H_2^{16}O$ ) with D atoms,  $^{16}O$  atoms and  $^{16}O_2$  molecules. Thick line: TPD profile of  $HD^{16}O$ , after 30 minutes of D irradiation of the water ice substrate. The water ice substrate is held at 10 K during all exposures. Traces are vertically shifted for clarity.

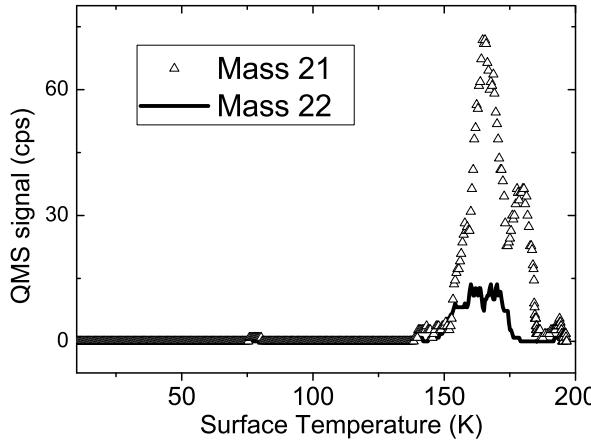
### 3. Results and Discussion

Several experiments have been performed. In the first one D-atoms were sent onto the water surface to confirm that hydrogen atoms do not react with water molecules in the substrate to produce deuterated water molecules (see the solid thick line in Fig. 1), as already mentioned by (Nagaoka et al. 2005). In addition, we determined that  $D_2$  molecules do not react with O-atoms nor with  $O_2$  molecules residing on the ASW ice surface. This, that may seem of secondary importance, is on the contrary a decisive result that proves that the water formation process requires hydrogen in atomic form.

Fig. 1 shows the mass spectrum recorded during the TPD performed after the irradiation of the water substrate with D-atoms and  $^{16}O$ -atoms (and  $^{16}O_2$  molecules). Water formation clearly occurs as is testified by the presence of  $D_2^{16}O$  and  $HD^{16}O$  peaks. These findings are not surprising although one could expect that  $D_2O$  should be mainly formed, because D is used as precursor. But it is also known that during the heating, isotope exchange between water molecules will occur (Smith et al. 1997). For a very thin layer of deuterated water, a complete isotope exchange with the underlying  $H_2O$  substrate molecules is expected around 150 K. In such a context, even if  $D_2O$  is formed at 10 K, most of the deuterated water will desorb as  $HD^{16}O$ , as is observed in our experiments.

Due to the mass spectrometric detection method of water molecules in the gas phase one could wonder whether molecules synthesized by the reaction of D-atoms and O-atoms and  $O_2$  were formed during the warm up of the whole ice substrate, a fact that would render the result not relevant to interstellar space. However, this is certainly not the case because reactions involving D-atoms must proceed at temperature below 20 K. At temperatures higher than that value the residence time of H/D-atoms becomes exceedingly small for reactions to occur.

In order to confirm unequivocally that water was formed starting from the reactants deposited from the gas phase and provide quantitative results, we repeated the experiment presented above



**Figure 2.** HD<sup>18</sup>O (open triangles) and D<sub>2</sub><sup>18</sup>O (solid line) desorption profiles after ten minutes of simultaneous irradiation of the amorphous H<sub>2</sub>O ice substrate with <sup>18</sup>O- and D-atoms.

with the oxygen beam line fed with <sup>18</sup>O<sub>2</sub> molecules. To be sure that the concentration on the substrate of D-atoms on the surface was always much higher than O-atoms and O<sub>2</sub> molecules, we opened the oxygen beam by time-slices of 20 s every 2 minutes while the D-beam was constantly running and irradiating the target held at 10 K. Thus, the relative concentration on the surface consists of  $\geq 10$  D-atoms per O-nucleus (in atomic or molecular form). (Matar et al. 2008) have shown that D reacts very efficiently with O<sub>2</sub>, and that O<sub>2</sub> disappears from the surface in a one D for one O<sub>2</sub> fashion. In such a scenario, due to the very low mobility of O-atoms (Tielens & Hagen 1982) and O<sub>2</sub> molecules at the irradiation temperature and in the temperature range in which H- and D-atoms remain adsorbed on the substrate, it is reasonable to assume that O and O<sub>2</sub> surface concentration reflects the proportions in which they were produced in the beam. O-atoms have therefore a very low probability to form O<sub>2</sub> and to encounter O<sub>2</sub> molecules to form O<sub>3</sub>, especially because they react with D with a higher probability.

Fig. 2 shows a TPD mass spectrum obtained after a 10-minute dose (30 time-windows of 20 s every 2 minutes) of <sup>18</sup>O-atoms and simultaneous D-atom irradiation of the ASW ice substrate at 10 K. The two peaks at mass 21 and 22 can only be assigned to HD<sup>18</sup>O and D<sub>2</sub><sup>18</sup>O and this clearly shows again that formation of water molecules has occurred on the amorphous H<sub>2</sub>O ice substrate, namely, a realistic analogue of cosmic dust surfaces in dense clouds.

In Table 1 are shown the relative abundances (in terms of uncorrected ion counts) of the species detected during the TPD, and, in addition, the total number of oxygen nuclei (<sup>18</sup>O atoms and twice the number of <sup>18</sup>O<sub>2</sub> molecules) that have been exposed to the substrate during the irradiation phase. We have not performed here any correction (except the correction from the H<sub>2</sub>O substrate). As a preliminary remark, the signal at mass 23 is expected to be 0, and it serves as a good indicator of the level of noise. To evaluate the conversion efficiency of O-atoms into water molecules in our experiment, we may evaluate the ratio  $\alpha$  between the sum of mass 20 (<sup>18</sup>OD and H<sub>2</sub><sup>18</sup>O), mass 21 (HD<sup>18</sup>O), mass 22 (D<sub>2</sub><sup>18</sup>O) and the total amount of <sup>18</sup>O nuclei:

$$\alpha = \frac{M20 + M21 + M22}{\text{total } ^{18}\text{O}} = 0.76$$

**Table 1.** Surface area under TPD curves of different masses after the  $^{18}\text{O} + \text{D}$  experiment. Results of a statistical model are given as a comparison.

	Total $^{18}\text{O}$	Mass 19	Mass 20	Mass 21	Mass 22	Mass 23
Area (Cts.K)	$15000 \pm 1000$	$30000 \pm 2000$	$10000 \pm 500$	$1250 \pm 150$	$250 \pm 70$	20
Model	15000	31802	8076	1434	188	0

This ratio represents an upper limit to the formation of water molecules from  $^{18}\text{O}$  assuming that the contribution of  $\text{D}_2^{16}\text{O}$  to the signal at mass 20 is negligible, as we have actually seen above (Fig. 1).  $\alpha$ , however, is not 1. The missing  $^{18}\text{O}$  nuclei are likely to have partially desorbed during the reaction or ended up in the form  $^{18}\text{OH}$  radicals or even as  $\text{H}_2^{18}\text{O}_2$  (and its deuterated isotopologues).

The formation of water molecules through the  $\text{D} + \text{O}_2$  pathway has already been studied and confirmed experimentally by (Miyauchi et al. 2008; Ioppolo et al. 2008; Matar et al. 2008). In the present experiment, we can deduce a lower limit for the formation efficiency for the  $\text{D} + \text{O}$  pathway. Actually 60% of the available  $^{18}\text{O}$  on the surface is contained in molecules. We can then see that, even if we assume that the molecular pathway has a 100% efficiency, it is less than  $\alpha$  and a lower limit for water formation via the  $\text{D} + \text{O}$  pathway is about 0.16 (0.76 – 0.60). Therefore, if we define the formation efficiency via atoms as the ratio between the fraction of water molecules that certainly formed via the  $\text{D} + \text{O}$  route (0.16) and the fraction of O-atoms available (0.4), we obtain 0.4 as a lower limit for the formation efficiency. On the other hand we can also deduce an upper limit. If we assume that O and  $\text{O}_2$  react with equal probability with D, we can estimate that 31% ( $0.76 \times 0.4$ ) of the water we have formed is the product of the  $\text{D} + \text{O}$  pathway and the efficiency of water formation via atoms is equal to  $\alpha$ . Considering both boundary conditions, we conclude that a reasonable estimate for the efficiency of water formation via atoms is about 0.5.

In order to know if we can go deeper in the understanding of the different pathways of water formation, we have made a very simple statistical model which is able to reproduce correctly the data (see Table 1). The model considers only statistical equilibrium. For sake of clarity we give here a simple example. Suppose there is an initial population of 90  $\text{H}_2\text{O}$  and 10  $\text{OD}$ , the final equilibrium obtained by randomly mixing the isotopes is  $\text{OD} = 0.5$ ,  $\text{OH} = 9.5$ ,  $\text{H}_2\text{O} = 81.225$ ,  $\text{HDO} = 8.55$ ,  $\text{D}_2\text{O} = 0.225$ . We have also included oxygen scrambling and calculated the statistical weight of all the final compounds. Finally, we sum the final products by masses taking into account QMS fractionation and are able to compare with the experimental results.

The question is the following: is it possible that the  $\text{OH} + \text{H}$  reaction has a activation barrier as previously suggested in gas phase. In this case,  $^{18}\text{OD}$  could be mixed with  $\text{H}_2\text{O}$  at higher temperature during the isotope exchange? We first assume that the  $\text{OD} + \text{D}$  reaction is actually negligible compared to the  $\text{O}_2 + \text{D}$  reaction, which leads to formation of  $\text{OD}$  and  $\text{D}_2\text{O}$  in equal amounts. Therefore, at the end of the D irradiation the ratio  $a = ^{18}\text{OD} / \text{D}_2^{18}\text{O}$  is equal to  $(40+30=70)/30$  because  $^{18}\text{O}$  atoms will form  $^{18}\text{OD}$  and  $^{18}\text{O}_2$  molecules will form an equal amount of  $^{18}\text{OD}$  and  $\text{D}_2^{18}\text{O}$  (via  $^{18}\text{O}_2\text{D}_2$ ). We assume only one adjustable parameter, the ratio  $b = ^{16}\text{O} / ^{18}\text{O}$  of atoms that will exchange during the TPD and statistically equilibrate their populations via isotope exchanges.

We find a best fit (Table 1) for the only free parameter  $b = 15$ . This means that the overlayer of products ( $^{18}\text{OD}$  and  $\text{D}_2^{18}\text{O}$ ) is mixed with 15 layers of the  $\text{H}_2\text{O}$  substrate and this is reasonably

consistent with previous results. (Smith et al. 2000) found an efficient mixing of about 50 ML of both isotopes, although they used a lower heating ramp and a different amorphous ice. If one believes in our simple statistical model, it is also possible to explain our data starting with an high population of OD, and therefore that an activation barrier for the OD + D reaction exists at 10 K. Indeed, the isotope exchange blurs the chemical pathways, and the data provided here give not enough constraints to make a firm conclusion about which pathway is more efficient. None the less, on average, we have estimated that water formation via the D + O pathway is highly efficient (about 50%) and certainly is responsible for producing a significant fraction of water molecules. More laboratory investigations should be performed and we actually plan to do that by combining TPD and infra-red spectroscopy.

The relevance of our results to astrochemistry is clear and gives strong experimental support to simulations of the formation and time scale of growth of water ice mantles in dense clouds. For the first time it is demonstrated on experimental grounds that water molecules can form on an amorphous water ice substrate under interstellar conditions (i.e., through surface reactions between atomic hydrogen and atomic and molecular oxygen on ASW ice), allowing the growth of icy mantles that are observed in dense clouds. Also, in our experiments, as occurs on interstellar grains, the formation of water ice via reactions between hydrogen and oxygen atoms suffers from the competition between the formation of molecular hydrogen and molecular oxygen and probably this competition might reflect in the depth profile inside the ice layer and in the time evolution of the mantle itself. Several issues still need to be investigated: the efficiency at various coverages and with an abundance ratio between hydrogen and oxygen atoms closer to the interstellar one; the interaction of the atoms that land from the gas phase and those belonging to the surface; other chemical pathways that contribute to the formation of water and so on. Besides all these investigations, of course, still to prove is how the first monolayer of water molecules may form efficiently on an amorphous silicate and/or and amorphous carbon layer. If it can not form efficiently enough, it will be compulsory to accept that the very first monolayer has to be built by water molecules formed by gas-phase reactions and then accreted on the bare refractory grain surface; a fact of major interest inside dense clouds near the threshold of observability of icy mantles. These and other issues will be addressed in forthcoming papers.

#### 4. Conclusions

We presented the first laboratory attempt to reproduce the formation of water molecules on of realistic space analogue of grain surfaces in dense molecular clouds. By exposing O- and D-atoms to an amorphous water ice substrate held at 10 K deuterated water molecules were formed with a high efficiency (~ 50 %).

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